

Kinetics of the Attack of Molybdenum by Dissociated Chlorine\*

by Daniel E. Rosner and H. Donald Allendorf

AeroChem Research Laboratories, Inc., Subsidiary of Pfaudler Permutit Inc.,  
Princeton, New Jersey 08540 (Received July 1965)

The true kinetics of the attack of molybdenum surfaces by both atomic and diatomic chlorine have been studied using microwave discharge-fast flow system techniques coupled with electrical resistance heating and monitoring of the reacting specimens. Experimental results are reported herein over the surface temperature range from 400°K to 1530°K, at reactant partial pressures of the order of  $10^{-3}$  to  $10^{-1}$  Torr. In contrast to the behavior of nickel, dissociation markedly increases the chlorination probability of molybdenum over the entire temperature range investigated, the enhancement being of the order of 100-fold at about 1000°K. The high reaction probability for  $\text{Cl}_2(\text{g})$  attack of high temperature nickel, previously reported by McKinley and Shuler, has been verified. When exposed to dissociated chlorine the ratio of the nickel chlorination rate to the Cl-atom recombination rate decreases with decreasing surface temperature-on 420°K nickel filaments the recombination coefficient  $\gamma$  has been found to be  $1/2$ . The implications of these results with regard to dissociative adsorption and evaporation on/from nickel and molybdenum surfaces are discussed in the light of available kinetic and thermochemical data for these and related heterogeneous reactions.

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Introduction

Dissociative adsorption on either metal surface sites or chemisorbed halogen atom monolayers plays a major role in determining the observed kinetics of the high temperature heterogeneous reactions between metals and the gaseous diatomic halogens  $X_2$  ( $= Cl_2, Br_2, \dots$ ).<sup>1-4</sup> While many such reactions (e.g., the chlorination of copper<sup>5</sup> and nickel<sup>1,6</sup>) have been reported to occur with very high reaction probabilities ( $\epsilon > 10^{-1}$ ) over a wide temperature range, several (e.g., the reaction between platinum and iodine<sup>7</sup> and the molybdenum/chlorine reaction discussed below) exhibit much lower reaction probabilities, and correspondingly high activation energies. In view of these differences, a series of studies of the kinetics of high temperature metal halogenation reactions in partially dissociated gas mixtures has been initiated at this laboratory with the expectation that a comparison of the results with those obtained in undissociated gases will shed light on the relative importance of dissociative adsorption as a rate limiting step in this class of heterogeneous reactions. These data should also provide valuable information on the response of refractory metals in partially dissociated halogen-containing gas mixtures, such as occur in lamps and

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- (1) J. D. McKinley, J. Chem. Phys. 40, 120 (1964).
  - (2) J. N. Smith Jr. and W. L. Fite, Rarefied Gas Dynamics, Vol. 1, ed. by J. A. Laurmann (Academic Press, New York, 1963), p. 430.
  - (3) J. D. McKinley, J. Chem. Phys. 40, 576 (1964).
  - (4) J. D. McKinley, J. Chem. Phys. 41, 2814 (1964).
  - (5) L. Frommer and M. Polanyi, Z. physik. Chem. 137A, 201 (1928).
  - (6) J. D. McKinley and K. E. Shuler, J. Chem. Phys. 28, 1207 (1958).
  - (7) L. K. Tower, Advanced Energy Conversion 3, 185 (1963).

thermionic devices utilizing chemical transport reactions,<sup>7, 8</sup> and the combustion products of current and future generation solid propellants.

The experiments reported herein were designed to provide the first high temperature data on the attack of polycrystalline molybdenum by atomic chlorine under conditions such that the observed reaction rates (a) would not be falsified by reactant or product diffusional limitations<sup>9, 10</sup> and thermal accommodation effects and (b) could be directly compared with chlorination rates for diatomic chlorine on the same molybdenum surface using the same experimental techniques. Despite the rapidity of the Cl-atom attack, this has been accomplished at surface temperatures up to 1530°K by combining the conditions of low pressure, high pumping speed and small specimen size, as described below. In addition, we have determined the recombination coefficient for Cl-atoms on nickel, and confirmed the high reaction probability for Cl<sub>2</sub> on nickel filaments above 1000°K, first reported by McKinley and Shuler.<sup>6</sup>

### Experimental

The techniques used here are similar to those developed in our previous kinetic studies of the oxygen atom attack of molybdenum<sup>11</sup> and graphite,<sup>12, 13</sup> the principal differences being those necessitated in the area of chlorine atom detection.

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(8) H. Schäfer, Chemical Transport Reactions, trans. by H. Frankfort (Academic Press, New York, 1964).

(9) D. E. Rosner, AIAA J. 2, 593 (1964).

(10) D. E. Rosner, AeroChem TP-111, April 1965; I/EC Fundamentals (submitted).

(11) D. E. Rosner and H. D. Allendorf, J. Chem. Phys. 40, 3441 (1964).

(12) D. E. Rosner and H. D. Allendorf, CARBON (in press).

(13) D. E. Rosner and H. D. Allendorf, AIAA J. (in press).

Atom Production. As indicated schematically in Fig. 1, the apparatus consists of a part vycor, part pyrex vacuum flow system coupled to a 25 liter/sec mechanical pump (not shown). Metered argon/ $\text{Cl}_2$  gas mixtures (dilute in  $\text{Cl}_2$ ) are passed through a 2450 Mc/sec, 125 w. microwave discharge cavity,<sup>14</sup> 28 cm downstream of which the gas encounters the electrically heated filament being studied. Flow metering was accomplished using sonic flow orifices fabricated from jeweled watch bearings.<sup>15</sup> The  $\text{Cl}_2$  flow rate was calibrated using absorption by Indicarb<sup>16</sup> as the primary standard. Unless otherwise specified the static pressure level at the specimen location was maintained at 1 Torr, and the flow rate was maintained at 21.7 cc (STP)/sec. This corresponded to a linear velocity of approximately  $2 \times 10^4$  cm/sec in the discharge tube, or a residence time of 45  $\mu$  sec/cm

$\text{H}_3\text{PO}_4$  was used to poison the vycor walls of the discharge tube to the heterogeneous recombination of Cl-atoms.<sup>17</sup> At comparable pressure and gas compositions (and, at much lower flow rates) Ogryzlo<sup>17</sup> verified the production of Cl-atoms using a Wrede gage, the discoloration of silver mirrors, and the removal of Cl-atoms by homogeneous reaction with  $\text{NOCl}$  (using a calorimetric probe as the titration endpoint detector). Indeed, comparison of the chemical titration method with the output

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(14) Raytheon "Microtherm" Generator and cavity supplied by Opthos Instrument Co., Rockville, Md.

(15) D. E. Rosner, ASME Trans., Series D, J. Basic Eng. 84, p. 458 (1962).

(16) Fisher Scientific Co. acid absorbent.

(17) E. A. Ogryzlo, Can. J. Chem. 39, 2556 (1961).

of a calorimetric detector led to the conclusion that below 4 Torr Cl-atom recombination was solely responsible for the surface-catalyzed heating of nickel detectors at  $T \approx 400^\circ\text{K}$ . In the present experiments a nickel wire detector revealed that a tenfold variation in Cl-atom concentration (at detectable levels) was obtained through variations of the  $\text{Cl}_2$  mole fraction in the feed gas and changes in microwave cavity tuning. In most of the experiments reported below, the Cl-atom mole fraction was maintained at  $4.3 \times 10^{-3}$  and the initial  $\text{Cl}_2$  mole fraction in the feed was  $1 \times 10^{-2}$ . This condition corresponds to the dissociation of roughly 22 percent of the  $\text{Cl}_2$  molecules passing through the microwave discharge.

Reaction Rate. The technique used for following the rate of the heterogeneous chlorination reaction was to continuously monitor the resistance-time curve of an electrically heated filament and to relate this to the diameter reduction caused by the reaction of molybdenum to form volatile products.<sup>11</sup> The molybdenum filaments, of initial diameter 0.0381 cm (15 mils) and total length 3 cm., were electrically heated using a regulated dc power supply. Together with current measurements, the voltage drop across the central 0.55 cm of the filament was continuously monitored using spring loaded contacts (cf. Fig. 1) leading to a recording potentiometer. During a run the filament was maintained at constant surface temperature by manually altering the current in accord with an optical pyrometer output (for  $T > 900^\circ\text{K}$ ) or a thermocouple output<sup>12</sup> ( $T < 900^\circ\text{K}$ ), thereby allowing the decrease in filament diameter caused by the

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(13) A 0.0127 cm chromel-alumel thermocouple junction diagonally lashed (with spring loading) across the center of the reacting molybdenum filament was used for this purpose. As will be seen below, data at the upper end of this temperature range satisfactorily matched data obtained using optical pyrometer temperature control.

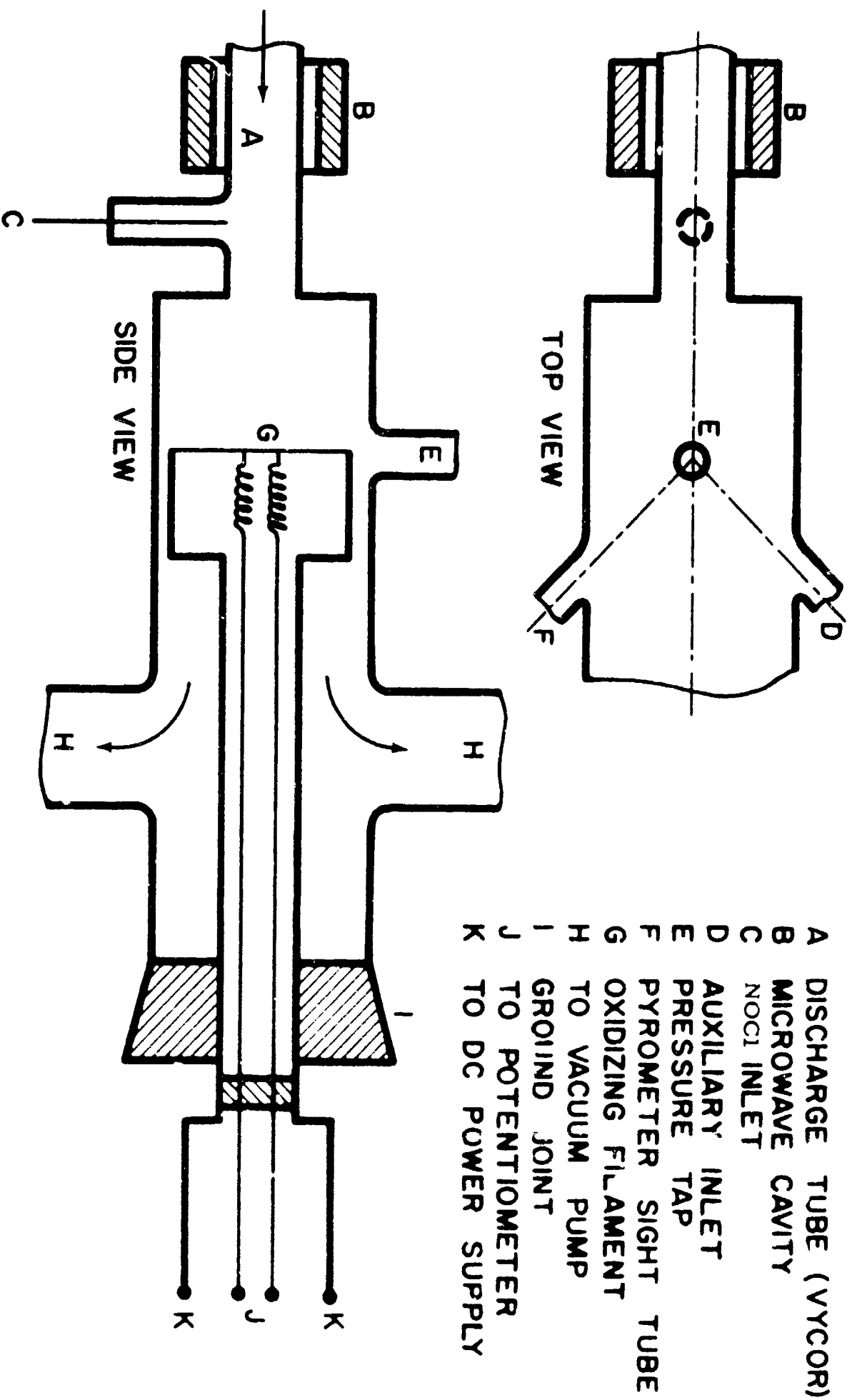


Figure 1. Filament chlorination apparatus.

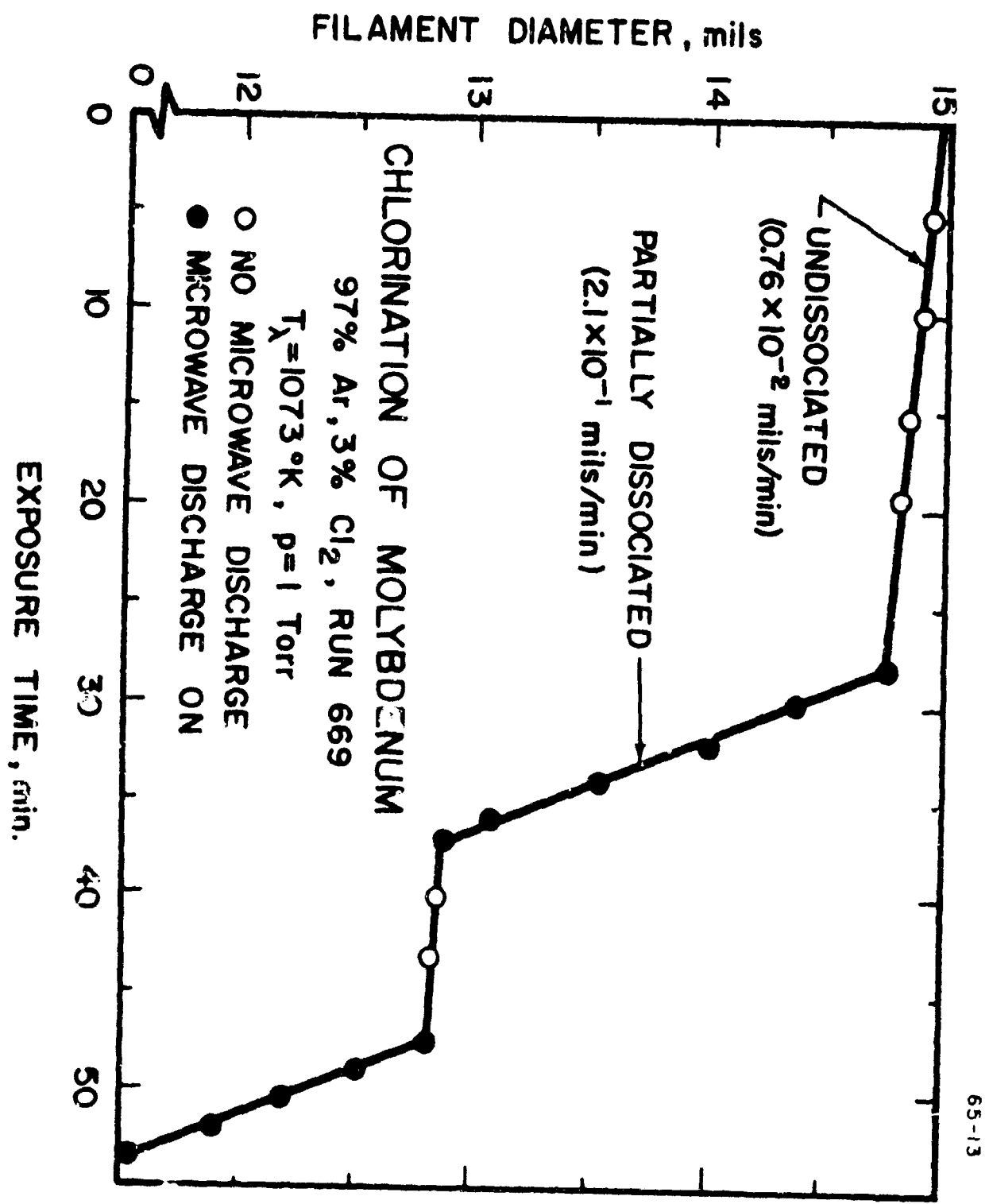


Figure 2. Effect of dissociation on the chlorination rate of molybdenum.

reaction (typically less than a total of 0.005 cm) to be related to the observed increase in electrical resistance. It should be stressed that while the optical pyrometer or thermocouple was used to maintain constant filament temperature during an experiment, the absolute value of the surface temperature, which in the present experiments was in the range 400 - 1530°K, was determined from the initial filament resistance in accord with its resistivity-temperature relation.<sup>19</sup> A typical plot of inferred filament diameter versus time is shown in Fig. 2, in which data for both undissociated and dissociated chlorine are included for comparison. In each case the reaction rate (proportional to the absolute value of the slope) is seen to be constant in time, as is to be expected for heterogeneous reactions forming volatile (non-protective) products. Owing to the large increase in reaction rate upon activation of the electrical discharge, and the small concentrations of Cl<sub>2</sub>(g) present, the observed reaction rate for the dissociated gas condition is fortunately dominated by the Cl-atom contribution, thereby necessitating only small corrections (typically less than 3 percent) for Cl<sub>2</sub> contribution.

Atom Detection. Owing to the high flow rates used it was not possible to utilize the NOCl titration to determine absolute Cl-atom concentrations. Instead, calorimetric techniques based on the heat release upon surface-catalyzed Cl-atom recombination were invoked.<sup>17,20</sup> Two types of nickel catalytic detectors were used, one for relative atom concentration determinations, and the other for absolute determination at

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(19) J. L. Everhart, W. E. Lindlief, J. Kanegis, P. G. Weissler and F. Siegel, Nat. Bur. Std. (U.S.) Circ. No. C447 (1943).

(20) D. E. Rosner, J. Amer. Rocket Soc. 32, 1065 (1962); see also L. Elias, E. A. Ogryzlo and H. I. Schiff, Can. J. Chem. 37, 1630 (1959).



at one flow condition. The first consisted of an electrically heated 0.0381 cm dia. nickel wire spanning the flow (at the molybdenum specimen location when the specimen was removed). In this case the atom concentration is taken to be proportional to the change in power required to maintain constant filament temperature ( $\sim 420^{\circ}\text{K}$ ) in the presence and absence of Cl-atoms.<sup>21</sup> Absolute atom concentrations were determined in a similar way, but using instead a 163 cm length of nickel wire wrapped in the shape of a cone (base dia. = 1.2 cm, altitude = 6.4 cm, apex downstream) mounted at the end of the discharge tube in such a way as to recombine all of the atoms passing through the tube into the test section. The observed power difference<sup>21</sup> was converted to Cl-atom concentration by assuming that each atom releases its thermodynamic heat of recombination at the nickel calorimeter surface. This measurements was repeated 7 times, with the result displaying a 7 percent average deviation from the mean. Confirmation that all atoms were removed from the stream was obtained based on comparisons with similar results using longer filaments (length = 237 cm) coiled in the same fashion.

Materials. All the data included herein were obtained using commercially available polycrystalline molybdenum (Westinghouse Lamp Div., Bloomfield, N. J., Type A, Process C3H) and nickel (International Wire Products Co., N. Y. C., Grade A)

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(21) Since the gas temperature (as measured by a poisoned glass covered thermocouple) is appreciably altered by the presence of the electrical discharge, as well as by the presence or absence of  $\text{Cl}_2$  when the discharge is on, the following modified procedure was adopted. The power required in the presence of a discharge through the  $\text{Cl}_2/\text{Ar}$  mixture was compared to the power required to maintain the same detector surface temperature in a pure argon discharge at the same flow rate, but with the tuning adjusted to maintain the same gas temperature.

filaments. High Purity Grade (Matheson) chlorine and Welding Grade (Air Reduction Corp.) argon cylinder gases were used without pretreatment. Static pressure at the filament location was measured using a U-tube manometer (equipped with a micrometer depth gage) containing dibutyl phthalate.

## Results

It will prove instructive to cast the experimental results for both the  $\text{Cl(g)}/\text{Mo(s)}$  and  $\text{Cl}_2(\text{g})/\text{Mo(s)}$  reactions in terms of dimensionless reaction probabilities. In the present case this can be done without a knowledge of the product gas species distribution by introducing the chlorination probability  $\epsilon$ , defined here as the ratio of the flux of molybdenum atoms (regardless of their chemical state of aggregation) away from the surface to the collision flux of  $\text{Cl(g)}$  or  $\text{Cl}_2(\text{g})$  with the surface. The molybdenum atom flux,  $Z''_{\text{Mo}}$ , is obtained from the observed rate of filament diameter change, the density of the filament (10.0 gm/cc) and the molecular weight of molybdenum (95.95 g/g-mole). The incident  $\text{Cl(g)}$  or  $\text{Cl}_2(\text{g})$  flux ( $Z''_{\text{Cl}}$ ,  $Z''_{\text{Cl}_2}$ ) is directly proportional to their known partial pressures, and is obtained from the Hertz-Knudsen equation evaluated at the filament surface temperature  $T$ :

$$Z''_i = \left( \frac{P_i}{kT} \right) \cdot \left( \frac{kT}{2\pi m_i} \right)^{1/2} \quad (1)$$

where  $i = \text{Cl}$  or  $\text{Cl}_2$ ,  $p_i$  and  $m_i$  are, respectively, the partial pressure and molecular mass of species  $i$ , and  $k$  is the Boltzmann constant. Thus, if  $Z''_{\text{Mo}}$  is experimentally found to be proportional to the  $n^{\text{th}}$  power of the chlorine partial pressure, where  $n$  is the reaction order, the probability  $\epsilon$  will be proportional to the  $n-1$  power of chlorine partial pressure (and, hence, independent of the latter when the reaction is first order, i.e., when  $n = 1$ ). It is also seen from Eq. (1) that the apparent activation energy

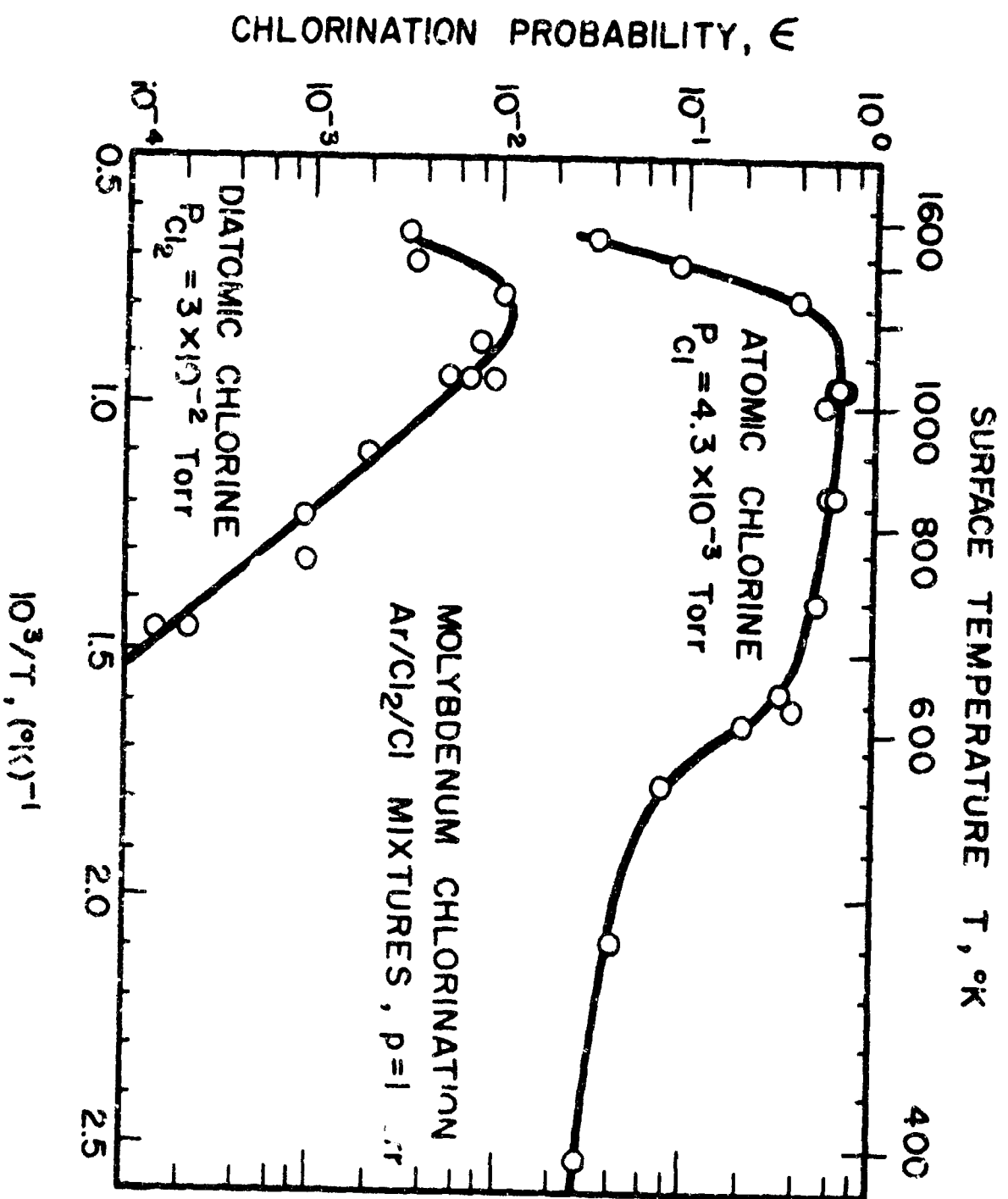


Figure 3. Chlorination probabilities for the attack of molybdenum by atomic and diatomic chlorine.

locally inferred from an Arrhenius plot of  $\ln \epsilon$  vs.  $1/T$  will exceed that obtained from a plot of  $\ln Z''_{(\text{Mo})}$  vs.  $1/T$  by the amount  $\frac{1}{2} RT$ , where  $R$  is the universal gas constant.

The Chlorination Probability and its Temperature Dependence. Figure 3

summarizes the results of 27 experiments on the chlorination probability as a function of molybdenum surface temperature, for both chlorine atom and chlorine molecule attack. It is clear that over the entire temperature range studied Cl-atom strikes are significantly more effective than  $\text{Cl}_2$  strikes in removing molybdenum atoms from the filament. Even at  $400^\circ\text{K}$  roughly one out of every 35 Cl-atom strikes is successful, and at temperatures near  $1000^\circ\text{K}$  the reaction probability attains values of the order of 2 out of every 3 collisions. In contrast, the  $\text{Cl}_2$  reaction probability (at  $p_{\text{Cl}_2} = 3 \times 10^{-2}$  Torr) never exceeded  $\sim 1/100$  and, at temperatures less than  $1000^\circ\text{K}$ , differed from the corresponding Cl-atom reaction probability by more than two orders-of-magnitude. Neither reaction probability displays simple Arrhenius (constant activation energy) behavior and each, in fact, exhibits a true maximum. However, this maximum is very shallow in the case of the Cl-atom attack, for which a temperature change of some  $400^\circ\text{K}$  produces no appreciable change in the reaction probability. At surface temperatures below about  $1100^\circ\text{K}$  the  $\text{Cl}_2$ -data can be represented by a straight line, corresponding to an observed activation energy of 13.7 Kcal/mole. For the Cl-data the observed activation energy varies continuously with temperature, and appears to pass through a maximum near  $600^\circ\text{K}$ .

Kinetic Order of the Cl-Atom Attack. A series of experiments was performed on 1050°K molybdenum filaments to determine the kinetic order of the Cl-atom attack mechanism in the range of maximum reaction probability. The Cl-atom concentration was varied over about a seven-fold range, as determined from the output of a 420°K nickel filament catalytic detector.<sup>21</sup> This produced the variations in chlorination rate ( $\propto Z''_{(\text{Mo})}$ ) shown in Fig. 4. Since these data are well represented by a straight line of unit slope (on log-log co-ordinates) one may conclude that the reaction order is unity under these conditions, and hence the maximum Cl-atom reaction probabilities, shown in Fig. 3 for the case  $p_{\text{Cl}} = 4.3 \times 10^{-3}$  Torr, would remain invariant with (at least comparable) changes in Cl-atom pressure.

Chlorination of High Temperature Nickel. McKinley and Shuler have reported<sup>6</sup> values for the reaction probability for the attack of nickel by diatomic chlorine of the order of<sup>22</sup> 1/2 at filament temperatures between 1200 and 1700°K, and at chlorine partial pressures of  $0.8 \times 10^{-1}$  to  $4 \times 10^{-1}$  Torr. If the  $\text{Cl}_2(\text{g})$  reaction probability on a nickel surface is indeed this high then one should not expect a drastic increase in reaction efficiency upon prior dissociation of chlorine. To test this prediction, and to confirm the results of Ref. 6, several experiments were performed on the chlorination of nickel filaments of the type previously used for atom detection. In this case the filaments were electrically heated to an estimated temperature of 1080°K in an argon/chlorine stream containing 1%  $\text{Cl}_2(\text{g})$  at a total pressure of 1 Torr. In the absence of a discharge the observed rate of diameter decrease ( $\sim 1.3 \times 10^{-4}$  cm/sec) indeed

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(22) Based on the filament temperature. The corresponding value based on the use of the upstream gas temperature in Eq. (1) was 1/5.

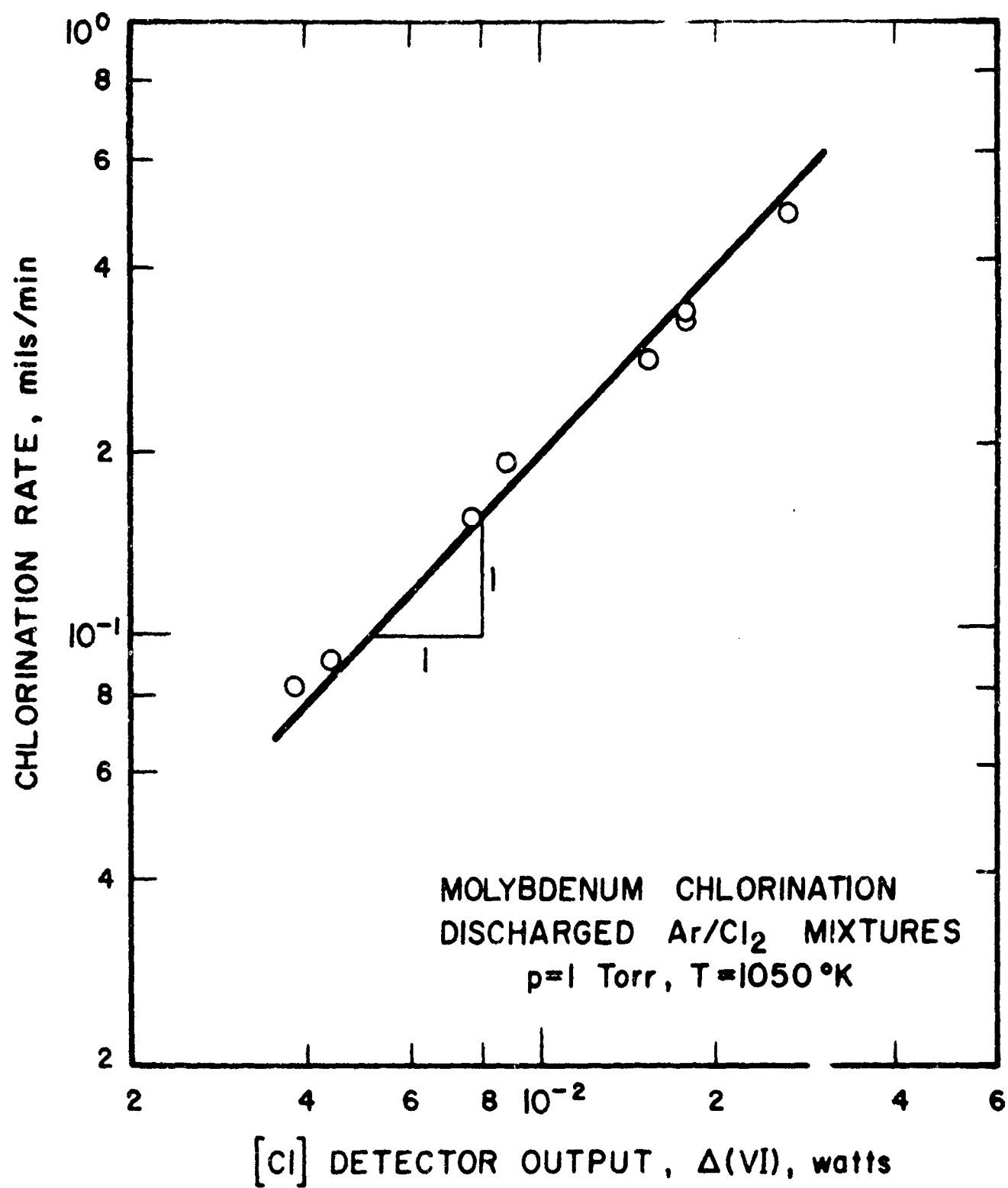


Figure 4. Kinetic order plot for the attack of molybdenum by atomic chlorine.

corresponded to a reaction probability of approximately  $1/2$ . Moreover, in contrast to the corresponding result for molybdenum (cf. Fig. 2), activation of the discharge produced virtually no change in the observed rate of diameter decrease. These results, which are consistent with those of Ref. 6, reveal significant differences between the nickel and molybdenum chlorination reactions.

Cl-Atom Recombination Probability on a Nickel Surface. The output of the relative atom concentration detector described earlier is proportional to the product of the recombination coefficient  $\gamma$  and the Cl-atom concentration. Consequently, an independent determination of the absolute Cl-atom concentration using the coiled nickel filament detector made possible the quantitative estimate  $\gamma \approx 1/2$  for Cl-atom recombination on a  $420^\circ\text{K}$  nickel surface. This result, when taken together with the observation that the nickel chlorination rate at this low temperature was not measurable, reveals that as the filament temperature is decreased recombination (rather than chlorination) becomes the favored fate for the Cl-atom. Similar trends apparently characterize the interaction of O-atoms with graphite,<sup>12,13</sup> i.e., the ratio of  $\epsilon$  to  $\gamma$  is an increasing function of surface temperature.

### Discussion

Identity of the Active Species. Based on the work of Ogryzlo<sup>17</sup> using similar atom production and detection techniques, as well as the data presented in Fig. 4, it is concluded that the observed reactivity of the chlorine passed through the microwave discharge is due to the presence of ground state ( $^2\text{P}_{3/2}$ ) Cl-atoms.

At comparable microwave power levels and pressures Ogryzlo<sup>17</sup> reported agreement between the Cl-atom concentration as determined from the quantitative gas phase titration reaction



and the output of a calorimetric nickel detector. While  $\text{Cl}_2$  ( $A^3\Pi_{ou}+$ ) has been identified in the products of chlorine discharges,<sup>23</sup> its presence here due to production in the discharge or by subsequent pre-association of ( $^2P_{3/2}$ ) Cl-atoms can be ruled out on the basis of residence time considerations.<sup>24</sup>

Finally, the fact that the observed chlorination rate increased linearly with the Cl-atom concentration inferred from the output of a nickel calorimeter detector (see Fig. 4) constitutes further indirect evidence that excited  $\text{Cl}_2$  molecules (written  $\text{Cl}_2^*$ ) play a negligible role in the present work. These experiments cover a two-fold range of initial  $\text{Cl}_2$  mole fractions, and were carried out at microwave power levels from 60 to 90 percent of full power. If excited chlorine molecules played a significant role both in the observed kinetics and in the nickel detector response, it is unlikely that a linear correlation would be observed over the resulting range of  $[\text{Cl}_2^*]/[\text{Cl}]$  ratios.

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(23) L. W. Bader and E. A. Ogryzlo, J. Chem. Phys. 41, 2926 (1964).

(24) The radiative lifetime of  $\text{Cl}_2$  ( $^3\Pi_{ou}+$ ) is shorter<sup>23</sup> than  $10^{-3}$  sec. Moreover, using termolecular rate constant  $k_{Ar} = 4 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  for the homogeneous recombination of Cl-atoms with argon as a third body (L. W. Bader and E. A. Ogryzlo, Nature 201, 491 (1964)) the residence time required for the initial Cl-atom concentration to fall to half of its original value would exceed 10 sec in the present experiments.



Absence of Transport Limitations. While reductions in the apparent activation energy of high temperature heterogeneous reactions are frequently associated with a local depletion of reactant due to physical limitations on its rate of supply (by convective diffusion),<sup>9, 10, 25, 26</sup> previous studies of the oxidation of molybdenum, tungsten and graphite at comparable reaction rates, reactant flow rates, surface temperatures and reactant partial pressures have demonstrated the absence of this class of physical phenomena in the present reactor.<sup>11-13</sup> Thus, reported reaction rates<sup>11-13</sup> are found to be independent of both reactant flow rate and identity of the carrier gas.<sup>26</sup> Consequently, the observed departures of the molybdenum chlorination probabilities from simple Arrhenius behavior are believed to be true kinetic phenomena, characteristic of the temperature and chlorine partial pressure levels encountered herein, and not peculiar to this particular reactor configuration.

Mechanistic Considerations. If every incident  $\text{Cl}_2$  molecule produced one  $\text{MoCl}_2(\text{g})$  product molecule,  $\epsilon$  would be unity. Similarly, if every incident Cl-atom is used to produce one  $\text{MoCl}_2(\text{g})$  molecule  $\epsilon$  would be 1/2. When  $\epsilon$  is considerably below these values<sup>27</sup> it is clear that some chlorine is being reflected from the surface and/or is adsorbed but later evaporated as either  $\text{Cl}_2(\text{g})$  or  $\text{Cl}(\text{g})$  before chemical reaction can occur.

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(25) D. E. Rosner and H. D. Allendorf, J. Electrochem. Soc. 111, 759 (1964).

(26) D. E. Rosner and H. D. Allendorf, J. Electrochem. Soc. 112, 653 (1965).

(27) The corresponding values for the reaction product  $\text{MoCl}_3(\text{g})$  are 2/3 and 1/3, respectively.

Considering first the reaction of  $\text{Cl}_2(\text{g})$  with  $\text{Mo}(\text{s})$  and  $\text{Ni}(\text{s})$  we note that the molybdenum chlorination probability passes through a maximum and then falls off sharply at higher temperatures (cf. Fig. 3) whereas under similar conditions the nickel chlorination probability does not exhibit this feature.<sup>6</sup> This suggests that the chlorine adsorbed on molybdenum is more weakly bound, and thus more likely to evaporate<sup>28</sup> as  $\text{Cl}(\text{g})$  and  $\text{Cl}_2(\text{g})$ . This reduces the high temperature reaction probability

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(28) In the absence of adsorption heat data some insight into the relevant binding energies can be obtained from an examination of the relative bond strengths of the gaseous metal chlorides. At  $298.16^\circ\text{K}$  the dissociation energy of  $\text{NiCl}(\text{g})$  is given as 115 Kcal/mole (A. G. Gaydon, Bond Dissociation Energies (Chapman and Hall, 1953)). From the heats of formation of the tungsten chlorides  $\text{WCl}_n(\text{g})$  ( $n = 2, 4, 5, 6$ ) given in the JANAF Thermochemical Tables (Dow Chemical Co., Midland, Michigan), we estimate the  $\text{WCl}$  bond strength to be about 113 Kcal/mole. While a reliable value for the  $\text{MoCl}$  bond does not appear to be available, the tungsten value given here, and ratios taken from L. L. Quill, The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics (McGraw Hill, Inc., 1950) indicate a  $\text{MoCl}$  bond strength of about 99 Kcal/mole. For comparison, note that the  $\text{Cl-Cl}$  bond in  $\text{Cl}_2(\text{g})$  has a strength of only 57.1 Kcal/mole (cf. Gaydon, loc. cit) and the heat of sublimation of molybdenum is 155.5 Kcal/mole (T. L. Cottrell, The Strengths of Chemical Bonds (Butterworths, London, 1958)).

of molybdenum.<sup>29</sup> The large value of  $\epsilon$  for high temperature nickel also implies a high sticking probability when  $\text{Cl}_2(\text{g})$  is incident upon this surface, i.e., a significant fraction of incident molecules dissociatively adsorb on the Cl-atom covered nickel surface. With this combination of high sticking probability and low evaporation rate of unreacted chlorine, it is not surprising to find that prior dissociation of the incident chlorine causes no significant increase in the high temperature reaction probability of nickel.

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(29) While reliable data on the thermodynamics of the Mo/Cl system do not appear to be available, calculations of the partial pressures of  $\text{WCl}_n(\text{g})$  ( $n = 2, 4, 5, 6$ ),  $\text{Cl}(\text{g})$  and  $\text{Cl}_2(\text{g})$  in equilibrium with a tungsten surface can be made based on the JANAF Thermochemical Data. When this is done we find that the equilibrium  $\text{Cl}(\text{g})$  and  $\text{Cl}_2(\text{g})$  pressures become comparable to the imposed  $\text{Cl}(\text{g})$  and  $\text{Cl}_2(\text{g})$  pressures (in the present experiments) at surface temperatures in the range  $1050^\circ\text{K} - 1250^\circ\text{K}$ . At these and higher surface temperatures the reaction to form the stable metal chlorides is thus thermodynamically not favored. Further verification of this tendency is provided by similar thermodynamic calculations and experiments on the molybdenum/oxygen and tungsten/oxygen systems. In contrast to the chlorination reactions studied here, we expect and find that at comparable reactant partial pressures the oxidation probability of tungsten and molybdenum monotonically increases in precisely the temperature range in which the chlorination probability drops off. For the attack of molybdenum and tungsten by  $\text{O}_2(\text{g})$  these kinetic measurements extend to a surface temperature of  $2600^\circ\text{K}$  (D. E. Rosner and H. D. Allendorf, AeroChem TN-61, May 1964; DEC AD 433 927).

In the case of molybdenum, however, the sticking probability is apparently low and the evaporation rate of unreacted chlorine larger. Prior dissociation can therefore greatly increase the overall reaction probability  $\epsilon$  in two distinct ways, viz. (i) by increasing the sticking probability, leaving the remainder of the reaction mechanism essentially unaltered, and (ii) by introducing a Rideal-type mechanism in which a Cl-atom from the gas phase can react directly with adsorbed chlorine atoms to form a complex leading either to the desorption of reaction product or diatomic chlorine.<sup>30</sup> Both of these mechanisms are readily reconciled with the observed first order kinetic behavior of this reaction (cf. Fig. 4).

Homogeneous Thermal Dissociation. At 1500°K the extent of Cl<sub>2</sub> dissociation predicted thermodynamically is appreciable. Indeed, based on the 1500°K equilibrium constant,  $p_{\text{Cl}} p_{\text{Cl}_2}^{-1/2} = 10^{-1.226}$ , the gas wetting the filament would contain a Cl-atom partial pressure of  $5.60 \times 10^{-2}$  Torr, even in the absence of a microwave discharge. At first sight this casts doubt on the significance of the data in "undissociated chlorine" at these filament temperatures. However, while it is likely that the gas temperature is raised locally to the filament surface temperature,<sup>31</sup> it is unlikely that adequate

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(30) It is anticipated that the relative importance of these routes can be assessed by independent measurements of the atom recombination probability on high temperature reacting surfaces, or transient measurements of the average residence time of a Cl-atom on the surface (when the specimen is subjected to a modulated atomic beam, in the spirit of Ref. 2).

(31) Since the filament diameter is of the order of 10 times the mean-free-path of the gas, molecules approaching the filament make an appreciable number of collisions with molecules which have either already interacted with the filament, or collided with those that have.

time is available for homogeneous dissociation in the vicinity of the filament. This can be verified by comparing the residence time for a gas molecule within the thermal layer of the filament (at most of the order of  $d^2/D_{\text{Cl}_2-\text{Ar}}$ , where  $d$  is the filament diameter and  $D_{\text{Cl}_2-\text{Ar}}$  is the Fick  $\text{Cl}_2$ -Ar interdiffusion coefficient) to the characteristic time  $(k_{\text{d,Ar}} n_{\text{Ar}})^{-1}$  for homogeneous  $\text{Cl}_2$  dissociation (where  $k_{\text{d,Ar}}$  is the appropriate dissociation rate constant<sup>32</sup> and  $n_{\text{Ar}}$  is the argon molecule number density). Since the residence time is found to be too small by more than five orders of magnitude, we are led to the conclusion that even at the highest filament temperatures investigated Cl-atoms were effectively absent as a potential reactant in all chlorination experiments carried out with the electrical discharge off.

### Conclusions

Based upon the experimental data and the discussion above the following conclusions may be drawn:

1. A convenient experimental technique, making use of a microwave discharge, a fast-flow subatmospheric pressure system and resistance heating/monitoring of the specimen, has been developed to study the true kinetics of rapid metal chlorination by both  $\text{Cl(g)}$  or  $\text{Cl}_2(\text{g})$  at partial pressures of the order of  $10^{-3}$  Torr and greater. The molybdenum and nickel chlorination reactions occur at constant (time-independent) rates, as expected for reactions forming volatile (nonprotective) products.

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(32)  $k_{\text{d,Ar}} \sim 10^8 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  at  $1500^\circ \text{K}$  (cf. H. Hiraoka and R. Hardwick, J. Chem. Phys. 36, 1715 (1962)).

2. The high reaction probability ( $\sim 1/2$ ) of  $\text{Cl}_2(\text{g})$  on nickel at surface temperatures above  $1000^\circ\text{K}$ , first reported by McKinley and Shuler,<sup>1</sup> has been verified. Consistent with this result, partial dissociation of chlorine in the microwave discharge has no appreciable effect on the chlorination rate of nickel.
3. In contrast, with molybdenum Cl-atoms are considerably more reactive than diatomic chlorine over the entire temperature range investigated ( $400^\circ\text{K}$  -  $1530^\circ\text{K}$ ). Even at  $400^\circ\text{K}$  roughly one out of 35 Cl-atom strikes is successful in removing a molybdenum atom from the filament and at temperatures near  $1000^\circ\text{K}$  the reaction probability (which is independent of Cl-atom concentration) attains values of the order of 2 out of every 3 collisions. Corresponding reaction probabilities for  $\text{Cl}_2(\text{g})$  attack of molybdenum never exceeded  $\sim 1/100$  (at  $p_{\text{Cl}_2} = 3 \times 10^{-2}$  Torr).
4. These results suggest that the sticking probability for  $\text{Cl}_2(\text{g})$  dissociative adsorption on (chlorine atom covered) nickel is much larger than on (chlorine atom covered) molybdenum. In the presence of  $\text{Cl}(\text{g})$  this kinetic difficulty on molybdenum is circumvented and a new (Rideal type) mechanism involving reaction as a result of direct gas phase atom strikes also becomes available.
5. Above about  $1200^\circ\text{K}$  the molybdenum chlorination probability (for both attack by  $\text{Cl}(\text{g})$  and  $\text{Cl}_2(\text{g})$ ) decreases with increasing surface temperature, indicating appreciable evaporation of  $\text{Cl}_2$  and/or  $\text{Cl}$  from the filament at these temperatures. The corresponding behavior for the oxidation of molybdenum and tungsten by  $\text{O}_2(\text{g})$  has not been observed at temperatures up to  $2600^\circ\text{K}$ .

5. The recombination probability for Cl-atoms on  $420^{\circ}\text{K}$  nickel filaments is about  $1/2$ . As the surface temperature increases the ratio of the chlorination rate to the recombination rate increases sharply.

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LIST OF FIGURE TITLES

<u>Fig. No.</u>	<u>Title</u>
1	Filament chlorination apparatus
2	Effect of dissociation on the chlorination rate of molybdenum
3	Chlorination probabilities for the attack of molybdenum by atomic and diatomic chlorine
4	Kinetic order plot for the attack of molybdenum by atomic chlorine



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